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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of:

David E. Fenton, et al

PHOTOGRAPHIC FILM ELEMENT  
CONTAINING AN EMULSION WITH  
DUAL PEAK GREEN RESPONSIVITY

Serial No. 10/732,956

Filed 11 December 2003

Commissioner for Patents  
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Alexandria, VA. 22313-1450

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*Frieda Grinnell*  
Frieda Grinnell

*Sept. 20, 2005*  
Date

**DECLARATION UNDER 37 CFR 1.132**

I, Dr. Steven G. Link, hereby declare as follows:

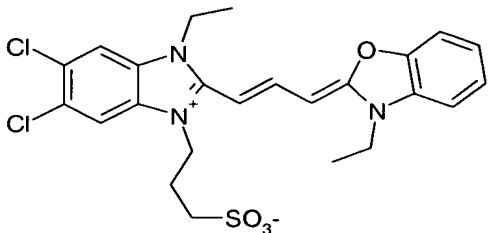
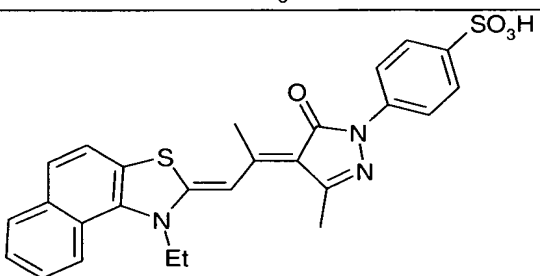
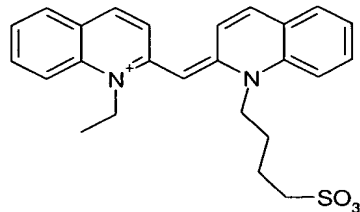
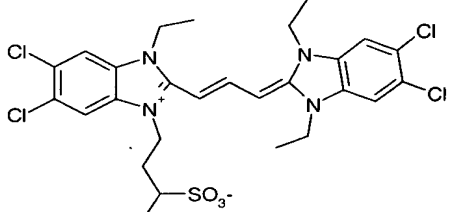
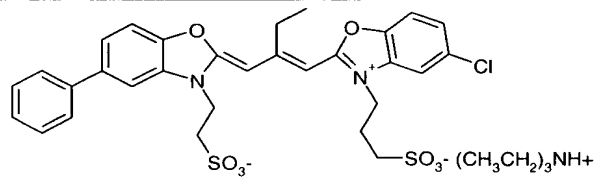
1. I have a Bachelor of Science degree in chemistry from Carnegie Mellon University, and a Doctor of Philosophy – Organic Chemistry from the University of Michigan. I have been employed by the Eastman Kodak Company for 28 years and hold 26 patents in the area of dyes used in imaging systems. My work at the Eastman Kodak Company has included the synthesis and testing of sensitizing dyes, spectral sensitization of emulsions for film products, commercialization of dyes for production, and laboratory head in charge of dye technology. I am an expert in the field of sensitizing dyes for photographic films and have given presentations at international conferences including, International Congress of Photographic Science, and the East-West Symposium II.

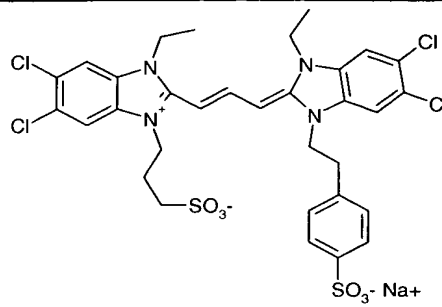
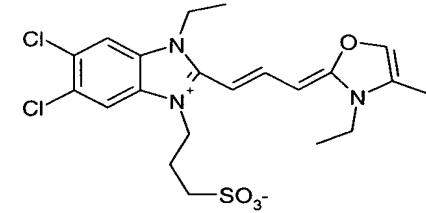
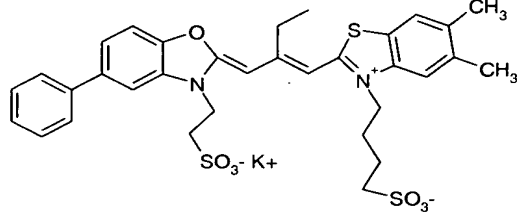
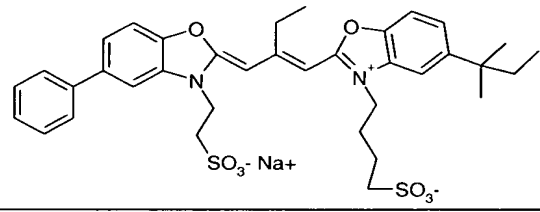
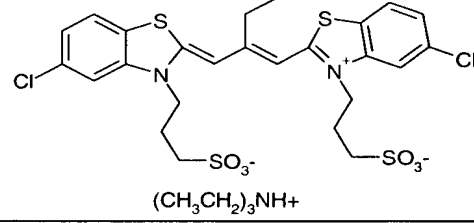
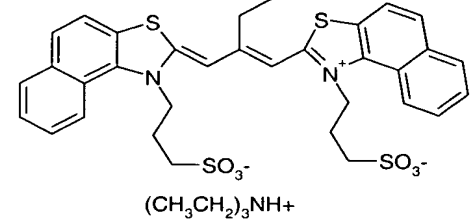
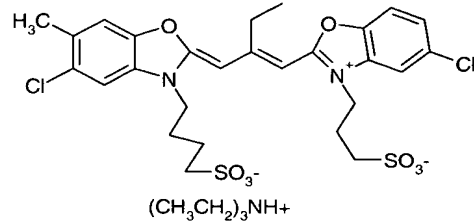
2. I am a co-inventor on U.S. Patent Application No. 10/732,956 and have read and understand the references cited against said Application.

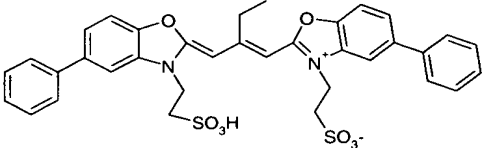
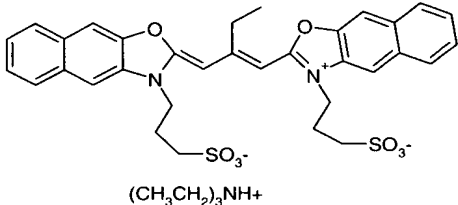
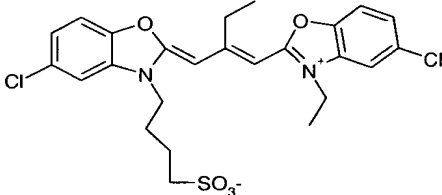
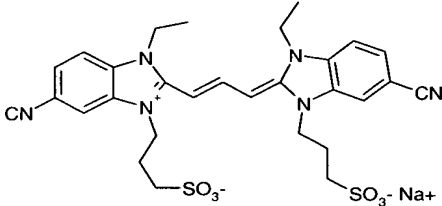
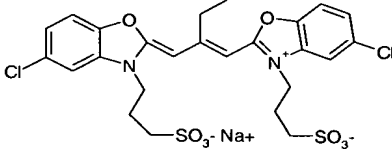
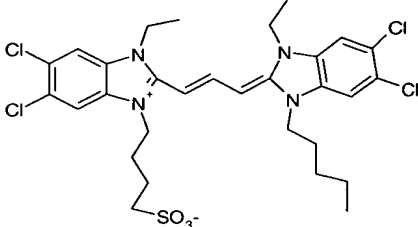
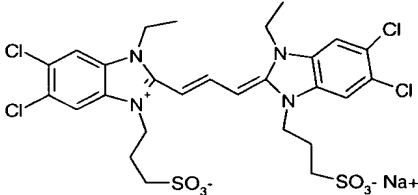
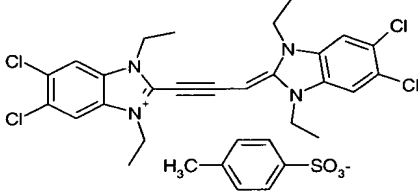
3. The following table lists dyes that are cited by the Examiner in the references. The wavelength for the maximum absorption of the J-aggregate is listed in column 3. This wavelength was obtained from a gelatin coating of a silver halide

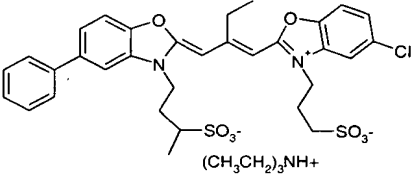
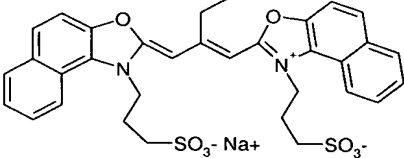
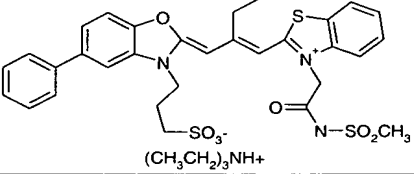
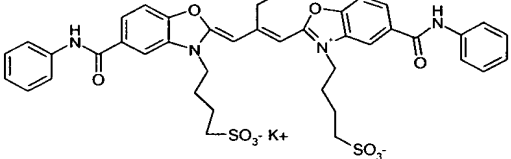
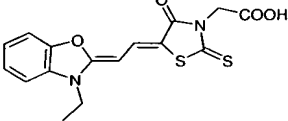
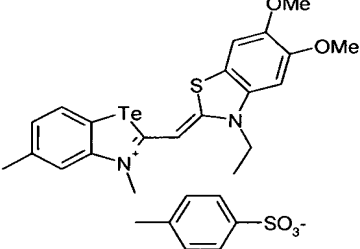
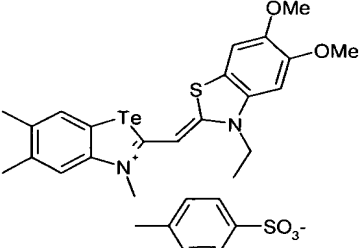
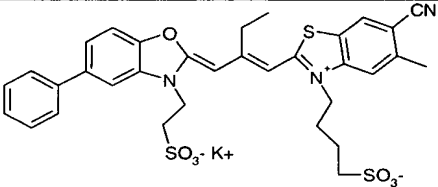
emulsion that has been spectrally sensitized with the dye. The coating was then placed in an integrating sphere attached to a scanning spectrophotometer. The total light transmitted by wavelength was plotted and the plotted spectrum was used to determine the maximum absorption. Not every dye in the table was available in our database for this tabulation. Values that are expressed as approximate ( $\sim$ ) are determined by comparing the exact dye in the table with a very close analog.

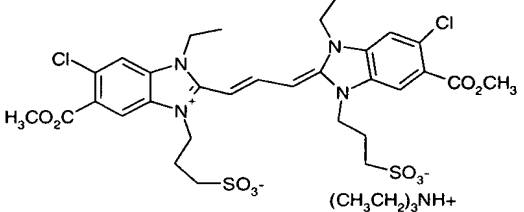
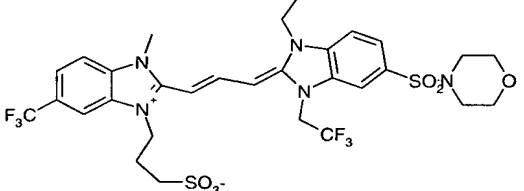
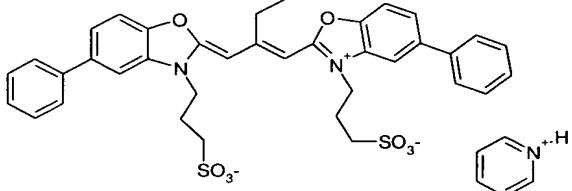
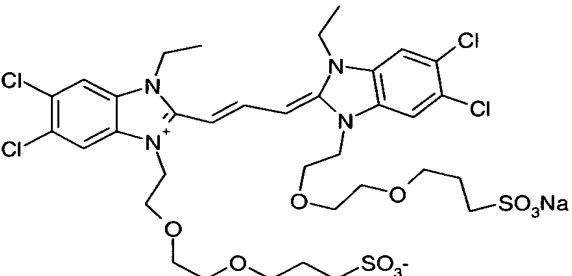
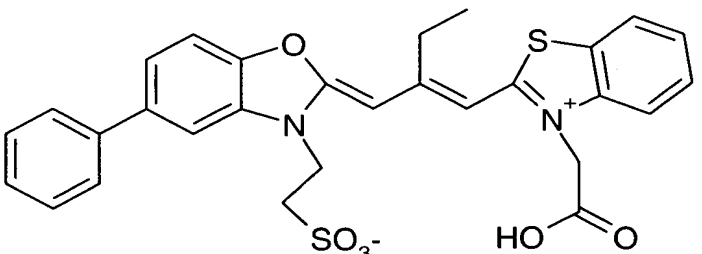
Table of Dyes and Their Aggregate Peak on Silver Bromide

	Dye	Aggregate Wavelength on AgBr	References
I		540 nm	Schwan '898
II		470 nm (H-aggregate)	Schwan '898
III		575 nm	Schwan '898
IV		575 nm	Schwan '898
V		546 nm	Sasaki '744 Sasaki '324 Nozawa '042 Ikegawa '748 Heki '226 Nagaoka

			'481
VI		~570 nm	Sasaki '744
VII		~530 nm	Sasaki '744 Sasaki '324
VIII		~595 nm	Sasaki '324 Nozawa '042 Ikegawa '748 Nagaoka '481
IX		~510 nm	Sasaki '324 Nozawa '042
X	 <p>(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH+</p>	650 nm	Nozawa '042
XI	 <p>(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH+</p>	667 nm	Nozawa '042
XII	 <p>(CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH+</p>	~525 nm	Ohtani '308 Ezaki '273 Heki '226 Shimba EP'315

XIII		545 nm	Ohtani '308 Ezaki '273 Ikegawa '748
XIV	 (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> NH <sup>+</sup>	573 nm	Ohtani '308 Ezaki '273 Heki '226
XV		~545 nm	Ohtani '308 Ezaki '273
XVI		582 nm	Ezaki '273 Heki '226 Shimba, EP '315
XVII		545 nm	Ikegawa '748 Shimba EP '315 Nagaoka '481
XVIII		~575 nm	Ikegawa '748 Nagaoka '481
XIX		575 nm	Ikegawa '748
XX	 H <sub>3</sub> C-C <sub>6</sub> H <sub>4</sub> -SO <sub>3</sub> <sup>-</sup>	524 nm	Sowinski '994

XXI		542 nm	Sowinski '994
XXII		567 nm	Sowinski '994
XXIII		565 nm	Sowinski '994
XXIV		525 nm	Sowinski '994
XXV		513 nm (broad)	Sowinski '994
XXVI		no aggregate	Sowinski '994
XXVII		no aggregate	Sowinski '994
XXVIII		~595 nm	Heki '226

XXIX		~580 nm	Heki '226
XXX		~545 nm	Heki '226
XXXI		548 nm	Ohashi '301
XXXII		~576 nm	Ohashi '301
XXXIII		~566	Nagaoka '481

4. Schwan '898 describes a spectral sensitivity with a single peak, not a sensitivity with one hypsochromic peak and one bathochromic peak. In column 12: 3-10, it states: "Preferably, a combination of dyes is chosen which imparts a maximum sensitivity to the emulsion layer at about 544 nm. The dyes advantageously impart a spectral distribution which results in a smooth, continuous curve which falls between curves UGH and TGJ of FIG. 2. Best results are obtained using two dyes having Formula I together with (1) a styryl dye, or (2) a merocyanine dye of Formula II." FIG. 2 of Schwan '898 clearly shows a single peak spectral

sensitivity with a maximum at 545 nm. Thus Schwan teaches that a maximum should occur where our invention specifies a minimum.

**In Layer 4 and layer 5**, a mixture of dyes is used, but the intent of the mixture is to achieve a smooth spectral sensitivity that fits the curve in FIG. 2. The maximum absorption wavelength of a mixture of dyes will be dominated by the dye that is used in the greatest quantity. The predominant dye of the mixture has a J-aggregate peak at 540 nm, and the other dyes are added simply to broaden the overall absorption around that peak. In this example dyes I, II, and XIX are used at a ratio of 5:1:2.5. The fact that dye I (J-agg at 540 nm ) is the majority of the mixture means this blend of dyes will not produce two peaks with a minimum near 545 nm, but a single peak near 540 nm.

*Example 13.* This example uses a mixture of dyes I, II, and III in a ratio of 3:1.33:1. Once again this produces a mixed aggregate with a single peak near 540 nm, the maximum absorption of dye I.

*Example 14.* This example uses a mixture of dyes I, II, and IV in a ratio of 3:1.33:1. Once again this produces a mixed aggregate with a single peak near 540 nm, the maximum absorption of dye I.

*Example 15.* This example uses a mixture of dyes I, II, and XIX in a ratio of 3:1.33:1. Once again this produces a mixed aggregate with a single peak near 540 nm, the maximum absorption of dye I.

*Example 16.* This example uses a mixture of dyes I, II, III, and XIX in a ratio of 3:1.33:1:1. Even though two long wavelength dyes are added in this example, the intent is to broaden the aggregate of dye I, not create two peaks.

5. Sasaki '744 describes a method of achieving additional green onto red interimage by adding an additional imaging emulsion layer to the film. The green spectral sensitivity of the film does not have two peaks, but a single peak that is near 545 nm. In col. 3, lines 27-30 it states: "wavelength weight-averaged between 500 nm and 600 nm ( ) of spectral sensitivity distribution of all green-sensitive layers is located in the range of 520 nm to 580 nm." The green sensitivities shown in Figures 1, 5, and 6 all show a single peak near 545 nm.

*Example 1, Samples 1 and 3.* These examples use a combination of dyes V and VI from Table I in the green-sensitive layers in a ratio of 2.5:1. Dye V has an aggregate absorption at 546 nm, so this combination will not produce a minimum in the sensitivity at 545 nm as our invention requires.

6. Sasaki '324 describes a similar invention to Sasaki '744 in more detail. It again calls for a weight-averaged green sensitivity in the range from 520 nm to 580 nm with a single peak. Close examination of Figures 8A and 8B reveals that all of the green sensitivities depicted there have a single peak, not two peaks. Indeed, the idealized green sensitivity depicted in Figure 11A shows a single peak is preferred near 545 nm. Thus, this patent teaches away from our invention that specifies a minimum in the sensitivity at 545 nm.

*Example 7.* Example 7 is a multilayer film with two green sensitive layers. The emulsions in those layers are sensitized with a blend of dyes V, VIII, and IX from Table I in a ratio of 3:1:5. These dyes have a range of sensitivities 546 nm, 595 nm, and 510 nm, respectively. However, it is clear that these dyes are blended to produce a single peak, not a double peak like our invention. This is evident from examining the inventive green spectral sensitivities from Figures 8A, 8B, and 11A.

7. Nozawa '042 describes a multilayer photographic film with a specific ratio of photographic speed at 560 nm. The object of this invention is to decrease the green sensitivity and red sensitivity of the film at 560 nm so there is less overlap between them. This minimizes the chemical color correction required to be built into the film, but limits the range of colors that can be reproduced. The fact that Nozawa seeks to decrease the green sensitivity at 560 nm argues against any desire to have two peaks in the green sensitivity, one shorter than 545 nm and one longer than 545 nm. In fact, Nozawa prefers a spectral sensitivity with a single peak at short green wavelengths as seen in the examples.

*Example 1, Sample 101.* Starting at col. 123:59, this example uses a ratio of dyes V, VIII, and IX from Table I in a ratio of 2.25:1:9 with wavelengths at 546 nm, 595 nm and 510 nm, respectively. This ratio of dyes with a high proportion of the dye absorbing at 510 nm is designed to produce a single peak at a short wavelength. There is not enough of the dye that absorbs at 595 nm to form a second peak at a longer wavelength.

*Example 1, Samples 107 and 108.* Sample 107 uses the same three dyes as sample 101, but with an even higher proportion of the short wavelength dye. Clearly this combination will not produce a spectral sensitivity with two peaks, one shorter than 545 nm and one longer than 545 nm. Sample 108, eliminates the long wavelength dye entirely and cannot result in a spectral sensitivity with two peaks.

*Example 2, col. 128:30-38.* This example uses the same three dyes but with a higher proportion of the 546 nm dye. Thus this example with equal amounts of the 510 nm dye and the 546 nm dye would not be expected to have a minimum at 545 nm as our invention requires.

8. Ohtani '308 describes a multilayer color photographic film with a specific spectral sensitivity distribution to render more accurate color reproduction under fluorescent lighting. Ohtani seeks to achieve this by moving the red sensitivity to shorter wavelengths as described in col. 3:13-21. The red sensitivity maximum is specified as being between 600 and 640 nm with the sensitivity reduced to 50% between 645 and 659 nm. As described in the introduction section, this will increase film sensitivity to the red phosphors of the fluorescent lights, but will not solve the overexposure to green light. Ohtani describes a single peak for the green sensitivity, col. 3:6-12, with a peak sensitivity between 530 nm and 590 nm such that the sensitivity will drop to 80% between 520 and 550 nm on the short wavelength side and between 550 and 600 nm on the long wavelength side. Taken together, this implies a single peak near 550 nm for the green sensitivity, the opposite of what our invention teaches.

*Example 1.* In the seventh layer of this example, only dye XII from Table I is used. This dye sensitizes at 525 nm, therefore the sensitivity of this layer will have only one peak near 525 nm. In the eighth and ninth layers, a combination of dyes XIII, XIV, and XV are used. These dyes have aggregate absorptions at 545, 573, and 545 nm, respectively. Therefore, these layers cannot have a peak shorter than 545 nm because none of the dyes has a peak shorter than 545 nm.

9. Ezaki, like Ohtani, seeks to use a short wavelength red spectral sensitivity to enhance color reproduction. It does not specify any spectral sensitivity distribution for the green sensitive emulsions.

*Example col. 66:1 to 77:15.* The highly sensitive and moderately sensitive green layers in this example both use a combination of 4 sensitizing dyes, dyes XIII, XIV, XV, and XVI from Table I. The wavelengths for these dyes are 545, 573, 545, and 582 nm, respectively with the largest portion of the mixture comprised on dyes XIII and XIV with wavelengths at 545 nm and 573 nm. Thus when these dyes are combined, they will not produce a spectral sensitivity with two peaks, one shorter than 545 nm and one longer than 545 nm.

10. Ikegawa '748 describes a multilayer photographic film with decreased stain due to retained sensitizing dye after processing. It does not describe any preferred spectral sensitization for the green sensitive layers.

*Example I, Sample 101.* The green sensitive layers of this example employ emulsions E, F, G, H, and I described in Tables I and II. These emulsions are sensitized with a mixture of dyes XVII and XVIII or a mixture of XVII, XVIII, and XIII. In each case, dye XIII is the predominant dye in the mixture and it has a maximum absorption at 545 nm. Therefore, these emulsions will have a peak sensitivity near 545 nm, and no short wavelength peak shorter than 545 nm.

11. Heki '226 describes a multilayer photographic film with a green-sensitive element which uses a dye set to give a double peak, one peak between 525 to 540 nm and another peak between 550 and 565 nm. There is no minimum level of absorption specified between the two peaks. All inventive examples use combinations of dyes V, XIV, XVIII, XXIX and/or XXX. This method provides a broadened green-sensitive spectral envelope much like that of US 5,053,324 and US 5,308,748 with maximum absorptions separated from the 546 nm fluorescent line but with substantial absorption remaining near the fluorescent 546 line.

*Example I, Samples 102, 103 and 104.* These samples, which form the basis for all the inventive examples' green-sensitizations, have 75 to 85 percent of the dye coming from dye V or XXX. Both of these dyes have absorption peaks near 545. Even when aggregated with small quantities of other dyes the absorption at the fluorescent 546 line is still substantial.

12. Both Sowinski '694 and Buitano '526 describe spectral sensitizations that are intended to reproduce the spectral response of the human eye. The green-light sensitivity of the human eye is very broad and peaks near 545 nm. The intent of the green-light sensitizations described in these patents is to use multiple dyes to produce a very broad relatively smooth spectral envelope. The patents claim a single peak, within the range 520 to 560 (Buitano) or 520 to 565 (Sowinski) and an absorption bandwidth at 50 percent of 50 nm (Buitano) or 65 nm (Sowinski). There are no minimum absorptions specified within these ranges. Because of the claimed peak positions and the claimed bandwidth all of these sensitizations have high levels of absorption at the fluorescent 546 line.

*Sowinski, Samples 101, 103 and 104.* These inventive samples have green peak sensitivities at 540, 541 and 564 respectively. Because of the bandwidth requirement all of these have high absorption at the fluorescent 546 line.

*Buitano, Samples 101 to 111.* These inventive examples all have peaks ranging from 528 to 558 and bandwidths at 50 percent absorptions ranging from 67 to 85 nm. All of these have high absorption at the fluorescent 546 nm line.

13. Shimba EP'315 describes a multilayer film designed to give improved color reproduction under fluorescent lighting. It specifies a range of spectral sensitivity in both the green and red light sensitive layers. The inventors attempt to improve color reproduction by moving the red sensitivity to shorter wavelengths and also by moving the highest green sensitive wavelength away from 545 nm. The green sensitivity is described as a *single peak* with a maximum between 520 and 570 nm with the proviso that the sensitivity at 545 nm can be no more than 80% the sensitivity at the peak. Still, a single peak is intended. The red maximum sensitivity is between 590 and 625 nm with a sensitivity at 610 nm that is more than 80% of the sensitivity at the peak. If Shimba were to combine the two-peak sensitivity described in our application with this very short red, the long-wavelength green peak would have a high degree of overlap with the red sensitivity and cause color contamination between the two records. Also, the green sensitive record, being above the red sensitive record, would steal light from the red record and cause a speed or granularity penalty. The intent of Shimba, as demonstrated in the examples, is to shift the red sensitivity to shorter wavelengths and shift the green sensitivity

slightly away from 545 nm, not to create a green spectral sensitivity with two peaks and a distinct minimum at 545 nm.

*Example 1, Sample 101 and 107.* In example 101 the green sensitive record uses dyes XII and XVII in a ratio of ~9:1. According to Shimba, this combination produces a green sensitivity with a maximum sensitivity at 553 nm on the emulsions used in the example. In sample 107, the amount of dye XVII is increased to 20%. Shifting the sensitivity to 556 nm and slightly lowering the sensitivity at 545 nm. This represents a shift in the peak of a co-aggregate of sensitizing dyes as the proportions are changed and in no way creates a second short wavelength peak as described in our application.

14. Ohashi '301 describes a short red spectral sensitivity in a multilayer film in combination with a specific interlayer interimage effect. The patent does not describe any requirements for the green sensitive record, and the examples do not describe green sensitivities with a short wavelength and a long wavelength peak.

*Example 101.* The dyes used in this example are dyes XXXI and XXXII in a 2:1 ratio. Since dye XXXI has a maximum absorbance at 548 nm and dye XXXII absorbs light at 575 nm, this combination of dyes cannot be used to create a spectral sensitivity with a short wavelength peak shorter than 540 nm. Ohashi '301 does not have an Example 7.

15. Sato '670 describes a color reversal multilayer film with improved color reproduction of certain blue and purple shades. The invention adds a layer to the film with a spectral sensitivity in the short blue region (<460 nm) that contains no yellow coupler. The purpose of this layer is to create an interimage effect specifically triggered by short blue wavelengths of light. There is no requirement for any green spectral sensitization. In fact, col. 55, line 4 states that the weight-averaged spectral sensitivity of the green record is 550 nm. There is no indication of any green spectral sensitivity with two peaks.

*Example 101.* This example is very confusing. As written, the green light sensitive emulsions use a combination of dye XVIII from the table above with several blue light absorbing dyes, S-6, S-7, and S-8. Emulsion K, used in the high speed green

sensitive layer, is said to use only dyes S-6, S-7, and S-8. All three dyes are blue light sensitizing dyes, and thus this emulsion would have no green sensitivity. Certainly none of these combinations would produce a green spectral sensitivity in accordance with our application.

16. Nagaoka '481 describes a color reversal multilayer film containing an extra green sensitive layer for interimage correction and better reproduction of certain colors. The main green light sensitive layers of the film have a standard green spectral sensitivity that is defined as a single peak between 500 nm and 570 nm. The extra layer for interimage must have a peak between 490 nm and 560 nm and must be different from the main green sensitivity maximum by 5 to 80 nm. This film does not have a green spectral sensitivity in the magenta color-forming layers with two peaks.

*Example 1 Sample 101.* The green sensitive emulsions in this example all use a combination of dye V (546 nm) and/or dye XVII (545 nm) with several different long green dyes (566-590 nm). No short wavelength green dyes are used in this example. Furthermore, dyes V and XVII always make up at least two-thirds of the dye combination, so the spectral sensitivity of these emulsions will be close to 545-550 nm. They will not produce a green spectral sensitivity with two peaks, one at a short green wavelength.

Date: 19 Sep 2005

Steven G. Link

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# Spectral Sensitization of Emulsions for Improved Color Reproduction and Reduced Illuminant Sensitivity of Color Negative Films

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## Abstract

When the spectral sensitivity of an image capture film differs significantly from the eye sensitivity, some color reproduction error will result, as well as some increase in the sensitivity of the film to exposure under different illuminants. Spectral sensitizing dyes for silver halide emulsions should be chosen such that they efficiently utilize light in a multilayer film structure, yet attention must be given to the impact on color reproduction. Furthermore, it is important to have sufficient sensitivity at the wavelengths where common illuminants have emission maxima. This paper discusses factors to be considered when selecting sensitizing dyes for silver halide emulsions for the blue and red records of a color negative film.

## Introduction

Maxwell's principle states that any visual color can be reproduced by the appropriate combination of three independent color stimuli (primaries). The amount of each primary required to reproduce the spectral colors defines the three-color matching functions for those stimuli. Each set of primaries has a different set of color matching functions, and all color matching functions are related by linear transformation. A film having spectral sensitivities that correspond to a set of color-matching functions is capable of accurately recording color scenes, and will minimize color shifts in scenes exposed under varying or mixed illumination.

Although any set of color matching functions is equally capable of accurately recording colors, not all sets are equally practical to employ in the design of color recording films. Many sets of color matching functions have negative sensitivities. Silver halide films cannot readily achieve negative sensitivities so it is important to choose a set of color matching functions that are all positive. Furthermore, most sets of color matching functions have significant overlap between the red and green sensitivities. Optical screening by overlying layers in a color negative film reduces the amount of light available to expose a red record if it has significant sensitivity at shorter wavelengths. Accordingly, it is important to choose a set of color matching functions, which minimize the spectral overlap of the blue, green, and red sensitive layers. Figure 1 shows a set of narrowest color matching functions proposed by MacAdam<sup>1</sup> that are all positive and have single peaks for the blue, green, and red

sensitivities. The constraint of no negative lobes results in a large degree of overlap between the green and red curve.

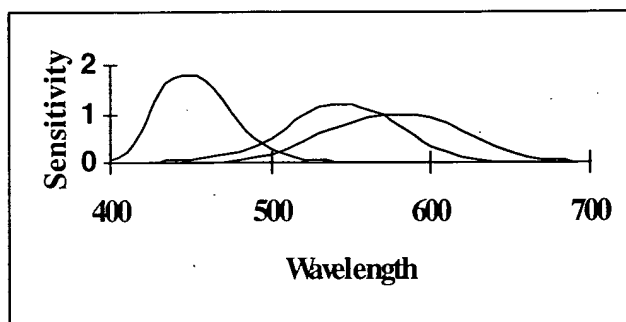


Figure 1. Spectral sensitivities that approximate color matching functions.

The accuracy of color recording for a film, and the amount of illuminant sensitivity it exhibits, is partly determined by how closely its spectral sensitivity approximates a set of functions like those shown in Fig. 1. The spectral sensitivity of the film is determined by the light that is absorbed by the individual emulsion components. Light absorption in the film is a function of the spectral absorption profile of the individual emulsion components modified by optical screening that occurs in the multilayer structure. The conventional film structure of blue sensitive layers over green sensitive layers over red sensitive layers necessarily filters shorter wavelengths of light before they reach the emulsions coated closest to the support. This places practical limits on how far the red sensitive layer can be shifted hypsochromically without incurring large speed penalties.

## Red Sensitive Emulsions

Figure 2 compares the light absorption of a long red and a short red sensitive emulsion with the red color matching function of Fig. 1. Although the long red emulsion (650 nm), is quite bathochromic to the red color matching function in Fig. 1, many films have been designed with such a red spectral sensitivity. The longer wavelength absorption increases the light absorbed by the emulsion in the multilayer structure and decreases the overlap with the green sensitive layer. As the chemical technology for silver halide films has improved over the years, it has become possible to use shorter red sensitive emulsions (625 nm) like that shown in Fig. 2. The light absorption of the short red emulsion is closer to the

red color matching function resulting in increased capability for accurate color recording. The short red emulsion sensitivity shown in Fig. 2 is a good compromise between the ideal color matching function and the capability of silver halide emulsion technology in a multilayer film structure.

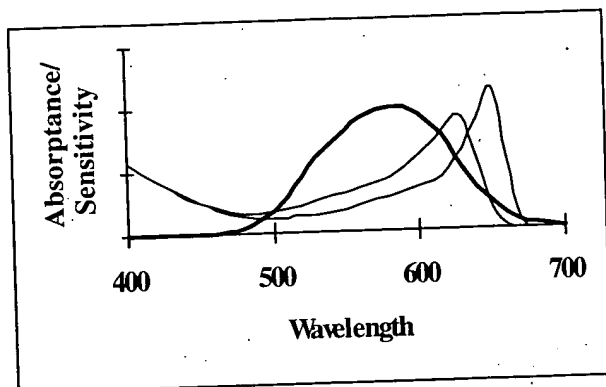


Figure 2. Comparison of a short red and a long red emulsion to the red sensitivity shown in Fig. 1.

### Blue Sensitive Emulsion

The blue sensitivity curve in Fig. 1 only slightly overlaps the green curve. With the blue recording layer on the top of a multilayer film structure, the indicated blue spectral sensitivity should be readily achievable. However, one must also consider the blue light absorption of the silver halide, the optical properties of various emulsion morphologies, and the blue spectral output of various light sources. Figure 3 shows the emission spectra of two common fluorescent lights and the spectral output of daylight. Note that the fluorescent lights have all of the blue energy concentrated in a narrow emission line at 435 nm. However, the output of daylight illumination is falling off at 435 nm. To achieve maximum speed under daylight exposure, an emulsion for the blue layer should be spectrally sensitized with a dye that absorbs at long blue wavelengths to absorb as much light as possible, but such a sensitization completely misses the fluorescent emission line at 435 nm. If, on the other hand, one chooses to sensitize the emulsion at 435 nm, there will be a speed penalty under daylight illumination relative to the long blue sensitive emulsion, simply as a result of the lower light intensity of daylight at 435 nm.

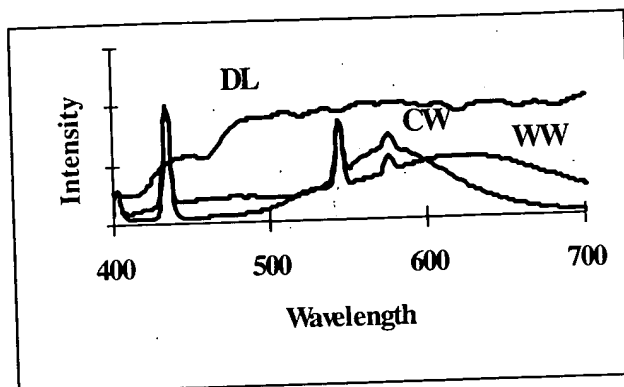


Figure 3. Spectral emission of 5500 K daylight (DL), cool white fluorescent (CW) and warm white deluxe fluorescent (WW).

When considering optics, it is also desirable to utilize tabular silver halide grains in the blue sensitive layer. These grains have much less optical scatter than three-dimensional grains. Because they tend to lie flat in the film plane, they also have a much higher degree of specular transmittance. The use of tabular emulsions in the blue sensitive layer thereby enables the transmission of red and green light to underlying layers with less degradation of sharpness. However, because tabular emulsions have low volume for their surface area, they have low intrinsic blue light absorption, which aggravates the problem with the 435 nm emission of fluorescent lights.

### Dye Selection - Red Sensitive Emulsions

The task of the emulsion scientist is to find spectral sensitizing dyes that will provide the desired 625 nm sensitivity without sacrificing photographic efficiency. The best sensitizing dyes from a light absorption perspective are the J-aggregating cyanine dyes. These dyes have narrow, intense absorption spectra that arise from a close-packed array of dye molecules on the surface of the silver halide crystal. However, if one considers the most widely used cyanine chromophores, it becomes clear that 625 nm sensitization is not easy to achieve.

The symmetrical cyanine chromophores have J-aggregates that absorb at wavelengths longer or shorter than 625 nm. The closest dyes are the unsymmetrical oxathia-carbocyanine dyes that generally form J-aggregates between 580 and 610 nm. Therefore, in order to dye an emulsion so that its wavelength of maximum absorption is approximately 625 nm, a mixture of dyes is required.

When two J-aggregating cyanine dyes are mixed, the resulting mixture can retain properties of the individual dyes or exhibit properties that are intermediate between the individual dyes. If the individual dye properties are retained, a J-aggregate of the "persistent" type is formed. When the mixture behaves like an average of the pure dyes, it is called a J-aggregate of the "amalgamation" type. This is analogous to the electronic states of mixed crystals.<sup>2</sup> It would be

desirable to achieve a 625 nm sensitization with a mixture of two cyanine dyes that form an amalgamation type aggregate. These aggregates have a single absorption maximum that is adjustable by changing the ratios of the two dyes. In Langmuir-Blodgett films of cyanine dyes, Yonezawa<sup>3</sup> has suggested that the amalgamation-type aggregate might be expected when the quantity  $\Delta_{DA}/T_{DA}$  is less than about 0.4; where  $\Delta_{DA}$  is the difference in energy of the J-bands for the individual dyes, and  $T_{DA}$  is the average of  $T_D$  and  $T_A$ , twice the energy difference between the monomer and J-aggregate transition for the donor and acceptor dye, respectively.

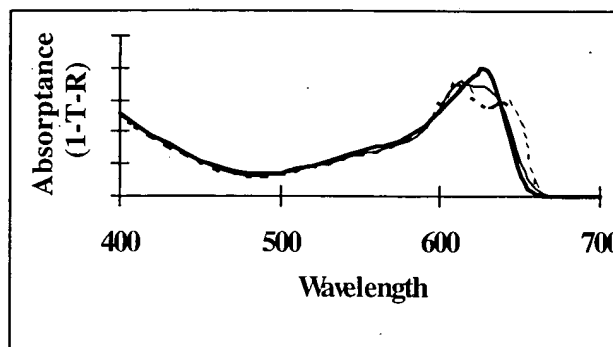


Figure 5. The effect of dye addition order for dyes 1 and 2 on the resulting absorption spectrum of the dyed, coated emulsion. Curve A (solid) - Dye 1 added first, then dye 2 after 15 min. Curve B (dashed) - Dye 2 added first, then dye 1 added after 15 min. Curve C (bold) - Both dyes added simultaneously and held 30 min.

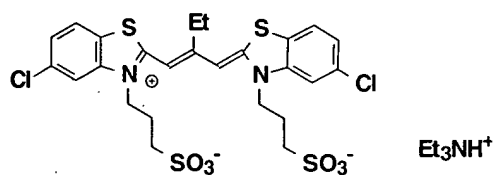
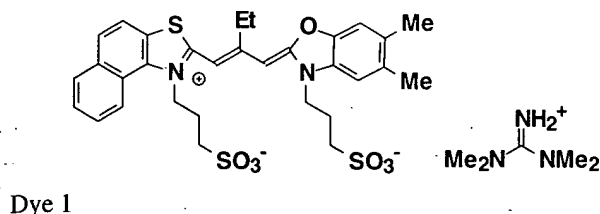


Figure 4. Two dyes which produce an amalgamation type J-aggregate.

The two dyes<sup>4</sup> in Fig. 4 have a  $\Delta_{DA}/T_{DA}$  value of 0.19 and might be expected to form an amalgamation type mixed aggregate. Dye 1 is an oxathiacyanine dye, and Dye 2 is a thiacyanine dye. A 2:1 molar ratio of these two dyes can be used to achieve an amalgamation mixed aggregate with a peak absorption at 625 nm. However, we have found that when adding dyes to a silver halide emulsion where they are strongly adsorbed, the proper energy relationships between individual dye aggregates is necessary, but not sufficient to form the desired amalgamation aggregate. In addition, it is also necessary to control the manner in which the dyes are added to the emulsion. When the dyes are added separately, the first dye will rapidly adsorb to the silver halide surface forming islands of pure aggregate before the second dye is added. The only way to achieve a uniform amalgamation aggregate is to add both dyes simultaneously.

This is demonstrated in Fig. 5, where the light absorbance spectra of coated emulsions are shown. Curve A shows the result of dyeing an iodobromide tabular emulsion with a 2 to 1 molar ratio of dyes 1 and 2 where dye 1 is added first, followed after 15 minutes by dye 2. Curve B shows the result for the opposite order of addition. Curve C shows the result for simultaneous addition of both dyes. Only in the third case is the desired amalgamation type aggregate obtained, demonstrating a single absorption peak.

### Dye Selection - Blue Sensitive Emulsions

In choosing sensitizing dyes for use on a blue sensitive tabular emulsion, it is important to balance the sensitivity for speed under daylight illumination, for electronic flash, and for sensitivity at 435 nm to record the fluorescent emission line. Two J-aggregating cyanine dyes can again be used, but, in this case, a mixed aggregate is not preferred. Instead, a long blue aggregate to absorb maximum light under daylight illumination should be combined with a short blue dye that aggregates as close to 435 nm as possible. The two dyes shown in Fig. 6 constitute such a pair of J-aggregating blue spectral sensitizing dyes. Like the red dyes, the long wavelength dye, Dye 3, is a thiacyanine dye that forms a sharp aggregate at 470 nm. Dye 4 is an oxathiacyanine that aggregates at 440 nm and has substantial absorbance at 435 nm. In this case the optimum performance for speed and illuminant response is obtained by adding the dyes separately to the emulsion and maintaining the individual dye aggregates on the surface.

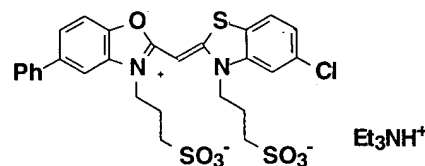
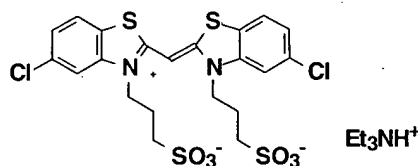


Figure 6. J-aggregating blue spectral sensitizing dyes.

## Film Spectral Sensitivity

Using red sensitive emulsions with a 625 nm maximum sensitivity and blue sensitive emulsions dyed with the two dyes shown in Fig. 6, it is possible to construct a multilayer color negative film with improved color recording accuracy and less illuminant sensitivity. The spectral sensitivity of two films with a long or short red spectral sensitivity is shown in Fig. 7. The film with the short red spectrally sensitized emulsions has a red sensitivity that is shifted 20 nm hypsochromic from the long red sensitivity at 650 nm. Figure 7 also shows the reflectance spectrum of the lobelia flower. Many blue flowers and certain fabric dyes have strong infrared reflectance. A film designed with long red sensitive emulsions records more of the infrared reflectance than the eye sees. This causes the color of the flower to be reproduced more magenta than it appears visually. The short red sensitive film records less of the infrared reflectance resulting in an improved capability to reproduce the color of the flower relative to its visual appearance.

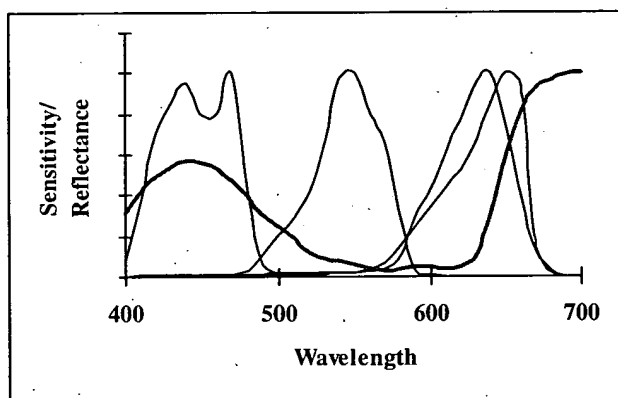


Figure 7. A multilayer film spectral sensitivity showing the shortened red response achieved with the mixed aggregate of dyes 1 and 2 in Fig. 4. The broad jagged line is the reflectance spectrum of the lobelia flower

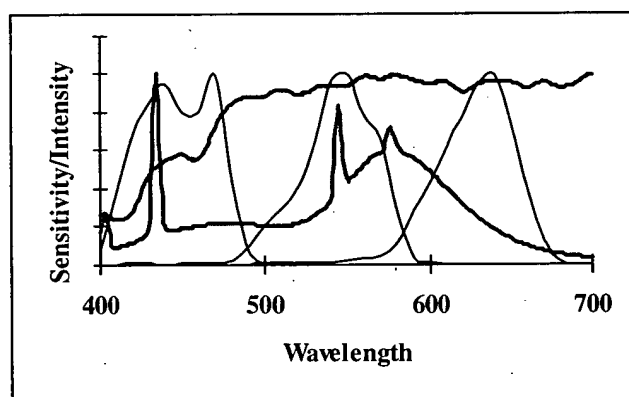


Figure 8. Film spectral sensitivity superimposed on daylight and cool white fluorescent illuminants.

Figure 8 shows the same film spectral sensitivity superimposed with daylight and cool white fluorescent spectral output. The short blue sensitivity overlaps the fluorescent emission line at 435 nm, while the long blue dye captures as much of the daylight output as possible. The shortened red spectral sensitivity also overlaps the red phosphor of the fluorescent light more efficiently than a long red spectral sensitivity. The combination provides less illuminant sensitivity to the film than a long red, long blue sensitized film would show.

## Conclusion

A shorter red spectral sensitivity than the traditional 650 nm sensitivity employed by many color films allows improved color reproduction by moving the peak closer to that of the human eye. The actual amount of hypsochromic shift will be limited in a practical sense because of screening of light by overlying layers in a multilayer film element. Because of the limited range of wavelengths where common cyanine dyes form J-aggregates, it is necessary to mix several dyes together to achieve the desired peak wavelength sensitivity. To achieve a true mixed aggregate on the surface of the silver halide grain, it is necessary to choose two dyes that have transition energies close together and to add the dyes simultaneously to the emulsion.

For sensitization of tabular silver halide emulsions in the blue spectral region it is also desirable to use two dyes, but in this case the optimum performance may be achieved by adding the dyes separately. A short blue dye with a J-aggregate absorption near 435 nm adds increased sensitivity at the emission line of fluorescent lights. An additional long blue aggregating dye absorbs light where the blue of daylight illumination is more intense, thus providing the highest possible blue speed.

The combination of a short red film sensitivity and a dual wavelength blue sensitivity offers improved color recording accuracy and reduced illuminant sensitivity compared to films with long blue/long red sensitivity only. The dual blue sensitization also enables the use of tabular emulsions in the blue layer of the film, which, in turn, improves the sharpness in underlying green and red layers.

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